$(H_3CNH_3)Al(SO_4)_2.12\text{-}H_2O$ with unit cell lengths 12·17 and 12·48 Å. Though 12·24 Å is the unit cell length value of ammonium alum, and due to the bulkiness of morpholinium ion, the cell dimension of morpholinium alum is expected to be greater than 12·24 Å, it is suggested that morpholinium alum is more densely packed.

The TG and DTA curves indicated that the dehydration started at 95° and was complete by 200°. The weight loss observed at this stage was 41·1% and that expected for the loss of 24 moles of water is 41·3%. The endotherm at 95° is attributed to the melting of the salt and those at 145° and 200° are due to the step-wise removal of water though it is not indicated in the TG curve under the conditions of the experiment. In a separate experiment about 200 mg of the double salt was heated up to 200° and was cooled to room temperature; within 24 hr the anhydrous salt regained all the lost 24 moles of water. Anhydrous salt gradually loses morpholinium sulphate with further increase in temperature and the residue around 600° was found to be $Al_2(SO_4)_3$. The weight loss observed at this temperature was 67% and that expected for the formation of $Al_2(SO_4)_3$ is 67·5%. The two endotherms at 395° and 530° are attributed to the decomposition of $(morphH)_2SO_4$; the former is due to the removal of H_2SO_4 and the latter is due to the decomposition of morpholine. $Al_2(SO_4)_3$ decomposes in the temperature range 700-860° to give Al_2O_3 as the end product. The final weight loss observed was 90% and that the expected for the formation of Al_2O_3 is 90·3%. The endotherm at 860° is due to the decomposition of $Al_2(SO_4)_3$ and the small exotherm at 900° is probably due to the phase transformation of $\gamma \rightarrow \theta Al_2O_3$ or $\delta \rightarrow \theta Al_2O_3$ according to Mackenzie and Berggern[3].

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Identification of a New Component of Cupric Calcium Sulphates of Bordeaux Mixture

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A new component $CuSO_4.2Cu(OH)_2.2Ca(OH)_2.2H_2O$ of cupric calcium sulphates (Bordeaux mixture), has been identified in addition to $CuSO_4.4Cu(OH)_2.6Ca(OH)_2.2H_2O$ reported earlier. These two components of Bordeaux mixture are blue in colour and form deep blue and bluish green carbonates in the weight ratio of 1 : 2.5 on passing carbon dioxide.

THE reaction between copper sulphate and calcium hydroxide in an aqueous medium using 0·75 eq. of lime and 1 eq. of copper sulphate was shown by Martin[1] to give a precipitate of tribasic cupric sulphate $[CuSO_4.3Cu(OH)_2.xH_2O]$. The X-ray studies and potentiometric titrations[2] of the precipitation reaction of 0·021*M* aqueous calcium hydroxide with 0·021*M* copper sulphate indicated the formation of stable compounds viz. $CuSO_4.3Cu(OH)_2$, $CuSO_4.4Cu(OH)_2$ and $5CuO.SO_3.2CaO.7H_2O$ at *p*H 6·20, 8·20 and 12·5 respectively. Sato[3] studied the reaction under normal atmospheric pressure which yielded precipitates having the compositions $CuSO_4.3Cu(OH)_2.2Ca(OH)_2.2H_2O$ along with free $CuSO_4.5H_2O$ when 20 moles of copper sulphate per 17 moles of calcium hydroxide were used; and $CuSO_4.3Cu(OH)_2.6Ca(OH)_2.2H_2O$ with free $Ca(OH)_2$ when 20 moles of copper sulphate were used for 21 moles of calcium hydroxide.

Since copper hydroxide has been known to form cupric hydroxy carbonates[4] in alkaline medium having different compositions, e.g. malachite green $CuCO_3.Cu(OH)_2$ and azurite blue, $2CuCO_3.Cu(OH)_2$, it was thought that the carbonation of the hydroxyl group of cupric calcium sulphates of Bordeaux mixture may result in the carbonates of its component salts. Hence investigations were carried out on the carbonated products of cupric calcium sulphates of the conventional Bordeaux mixture[5], obtained from copper sulphate pentahydrate and calcium hydroxide in the molar ratio of 1 : 0·297. The blue precipitate of cupric calcium sulphates of Bordeaux mixture on carbonation yielded two compounds having the formulae (a) $CuSO_4.2CuCO_3.2CaCO_3.2H_2O$ and (b) $CuSO_4.4CuCO_3.6CaCO_3.2H_2O$ and these corresponded to the respective compositions of (i) $CuSO_4.2Cu(OH)_2.2Ca(OH)_2.2H_2O$ and (ii) $CuSO_4.4Cu(OH)_2.6Ca(OH)_2.2H_2O$ in the original Bordeaux mixture. These compounds when present in Bordeaux mixture were both blue in colour and formed deep blue and bluish green carbonates respectively when treated with carbon dioxide and the *p*H value of the hydrogen reduced from 12·4 to 8·0. This observation demonstrates that these two compounds coexisted in the Bordeaux mixture as separate phases at the time the polybasic cupric calcium sulphate precipitated. After carbonation these compounds were separated by elutriation as their carbonates differed considerably in their bulk densities. Further, these compounds were found in the ratio of 1 : 2·5 by weight as a : b. The compound $CuSO_4.2Cu(OH)_2.2Ca(OH)_2.2H_2O$ which formed deep blue carbonate on carbonation, has been identified as one of the two stable components of Bordeaux mixture. The reaction in the case of the component identified can be written as:

$$3CuSO_4.5H_2O + 4Ca(OH)_2 \xrightarrow{H_2O} CuSO_4.2Cu(OH)_2.2Ca(OH)_2.2H_2O + 2CaSO_4.2H_2O$$

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Double Acetates of Pb(IV) & Sn(IV) Acetates

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Double acetates of composition $M_2'[M(OAc)_6].Ac_2O$ of Sn(IV) and Pb(IV) acetates and acetates of alkali metal, thallium and ammonium acetates have been isolated from acetic anhydride. Molar conductance, molecular weight and IR studies reveal two types of acetate coordination.

IN continuation of our studies on acetic anhydride as a polar solvent[1-6], we report now the preparation and characterization of the double acetates of Pb(IV) and Sn(IV) acetates and their behaviour in acetic anhydride.

Tetra-acetates of lead and tin are fairly soluble in acetic anhydride and the resultant solutions are non-conducting. The solubility of the acetates and the conductance of the solution increase enormously if ammonium or thallous acetate or the acetates of alkali metals are added to the solutions. Conductometric titrations between the tetra-acetates of tin and lead and the alkali metal acetates in acetic anhydride show two breaks in the conductance — composition curves corresponding to the formation of the complexes of composition $M(OAc)_5^-$ and $M(OAc)_6^{-2}$. When solvent ether was added to these solutions, compounds of the composition $M_2'M(OAc)_6.xAc_2O$, where x has a value between two and six, separated out. Stoichiometric compositions of these compounds have been determined by elemental analysis (Table 1). The solvent molecules are lost on heating the compounds to 150° under reduced pressure indicating that the solvent molecules are held loosely within the crystal lattice.

The compounds are stable in dry atmosphere but, when exposed to moisture, lead compounds become black in colour while the tin compounds become liquids. All the compounds have fairly high melting points. These are insoluble in benzene, carbon tetrachloride and chloroform but are soluble in nitromethane, nitrobenzene, acetonitrile and acetone. Molar conductance values of the millimolar solutions in nitrobenzene show them to be ionic in nature and the molecular weight determinations show them to be monomeric. Conductometric titrations of the compounds against hydrogen chloride in nitrobenzene show two breaks in the conductance-composition curves corresponding to the stepwise replacement of two acetates by chloride ions. Further addition of hydrogen chloride to the solution does not result in any significant change in the conductance suggesting that, in these complexes, two acetate groups are different from the four acetate groups and there is a complete analogy between $SnCl_6^{2-}$ and $Sn(OAc)_6^{2-}$ species in solution.

TABLE 1 — MELTING POINTS, ANALYTICAL AND CONDUCTANCE DATA OF DOUBLE ACETATES OF TIN(IV) AND LEAD(IV)

Compound	m.p. (°C)	Metal (%) Found	Metal (%) Calc.	Λ_M (nitrobenzene) (ohm^{-1} cm^2 mole^{-1})
$Li_2[Sn(OAc)_6]6Ac_2O$	100*	10·60	10·80	33·5
$Na_2[Sn(OAc)_6]4Ac_2O$	136*	13·05	12·80	39·1
$K_2[Sn(OAc)_6]4Ac_2O$	Above 200	12·05	12·38	27·6
$(NH_4)_2[Sn(OAc)_6]4Ac_2O$	39	13·24	12·94	24·3
$Li_2[Pb(OAc)_6]6Ac_2O$	97	17·10	17·43	26·4
$Na_2[Pb(OAc)_6]4Ac_2O$	87*	20·04	20·39	29·8
$K_2[Pb(OAc)_6]4Ac_2O$	133	20·06	19·77	36·2
$(NH_4)_2[Pb(OAc)_6]4Ac_2O$	60	20·21	20·59	21·7

*Melted with decomposition.

In the present compounds, there are two distinct types of acetate groups showing two types of asymmetric and symmetric carboxylate stretching frequencies. The absence of bands in the region 1590-1610 cm^{-1} rules out the possibility of the existence of any bridging acetate group in these compounds[7]. This is in agreement with their non-polymeric nature as indicated by molecular weight studies. Two absorption bands at 1570 and 1350 cm^{-1} assigned to νOCO_{as} and νOCO_s modes of the carboxylate group are observed which may be attributed to the unidentate nature of the acetate group[8,9]. The separation of the symmetric and asymmetric stretching mode of the carboxylate group is ~220 cm^{-1} suggesting that these acetate groups are covalently bonded to a good extent. The other symmetric and asymmetric carboxylate stretching modes are observed in the lower frequency region and the separation of the two modes is ~150 cm^{-1} (similar to that present in sodium acetate) which indicates a fair degree of ionic character.

The double acetates show an initial loss of alkali metal acetate during thermal decomposition and subsequently follow the same trend as proposed by Rao *et al.*[10]. There is no evidence to show the formation of oxycarbonate or lower acetates.

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